

**REPORT DOCUMENTATION PAGE**Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

<b>1. REPORT DATE (DD-MM-YYYY)</b> 28 March 2003		<b>2. REPORT TYPE</b> View Graphs		<b>3. DATES COVERED (From - To)</b>	
<b>4. TITLE AND SUBTITLE</b>  New Polynitrogen Compounds				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Jerry A. Boatz, Karl Christie, Ralph Haiges, Stefan Schneider, Thorsten Schroer, Ashwani Vij, William W. Wilson				<b>5d. PROJECT NUMBER</b> 2303	
				<b>5e. TASK NUMBER</b> M2C8	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b>  Air Force Research Laboratory (AFMC) AFRL/PRSP & ERC., Inc. 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  AFRL-PR-ED-VG-2003-076	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>  Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S NUMBER(S)</b> AFRL-PR-ED-VG-2003-076	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b>  Approved for public release; distribution unlimited.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b>					
<b>20030805 153</b>					
<b>15. SUBJECT TERMS</b>					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  A	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b> Sheila Benner
<b>a. REPORT</b> Unclassified	<b>b. ABSTRACT</b> Unclassified	<b>c. THIS PAGE</b> Unclassified			<b>19b. TELEPHONE NUMBER (include area code)</b> (661) 275-5963

FILE

MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

31 Mar 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-076**  
Karl Christe (AFRL/PRSP (ERC)); Ralf Haiges, Stefan Schneider, Thorsten Schroer (Loker  
Hydrocarbon Research Institute); Ashwani Vij, Vandana Vij, and William W. Wilson (AFRL/PRSP  
(ERC)), "New Polynitrogen Compounds"

AFOSR Molecular Dynamics Contractors Conference  
(San Diego, CA, 18-20 May 2003) (Deadline: 18 May 2003)

(Statement A)

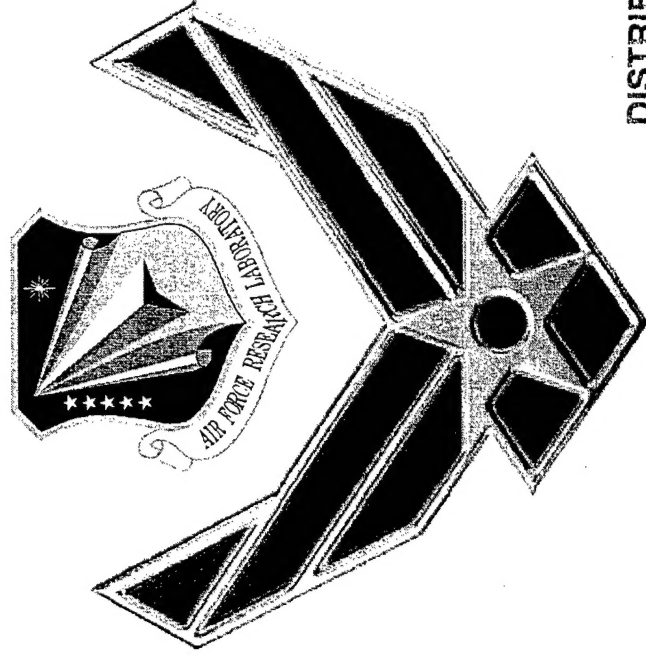
Boatz  
5364

Christe  
5194

# **Towards New Polynitrogen Species: The Search for Viable Precursors**

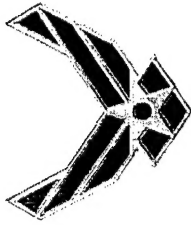
## **AFOSR Molecular Dynamics Contractors**

**Conference  
May 18-20, 2003**

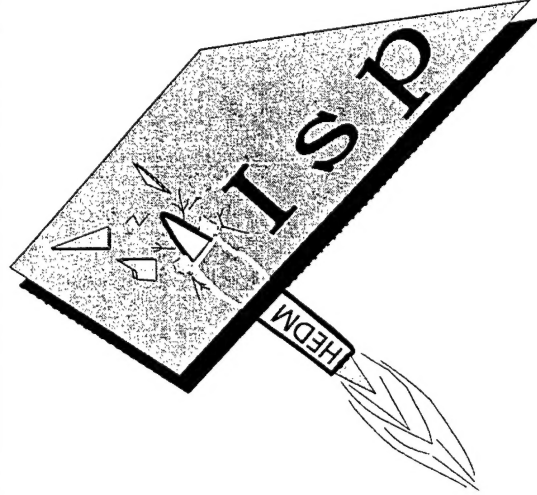


**Dr. Jerry A. Boatz**  
**Senior Research Chemist**  
**Propellants Branch**  
**Air Force Research Laboratory**  
**jerry.boatz@edwards.af.mil**  
**(661) 275-5364**

**DISTRIBUTION STATEMENT A**  
Approved for Public Release  
Distribution Unlimited



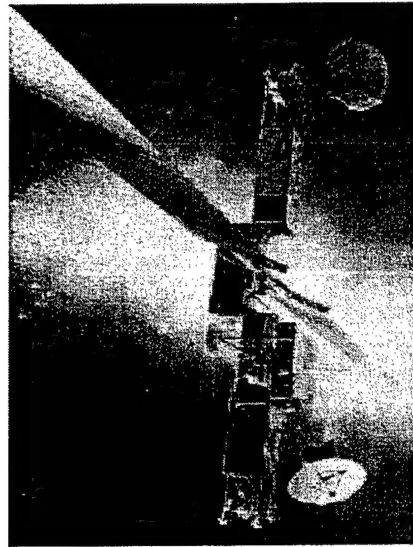
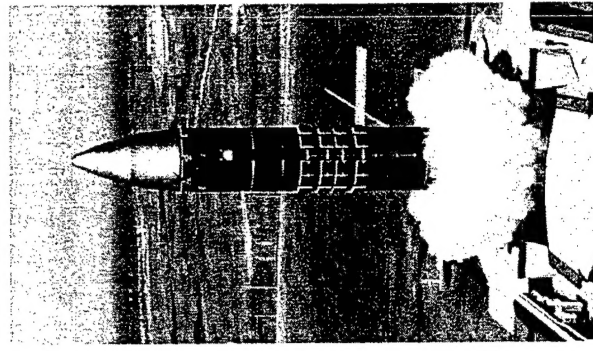
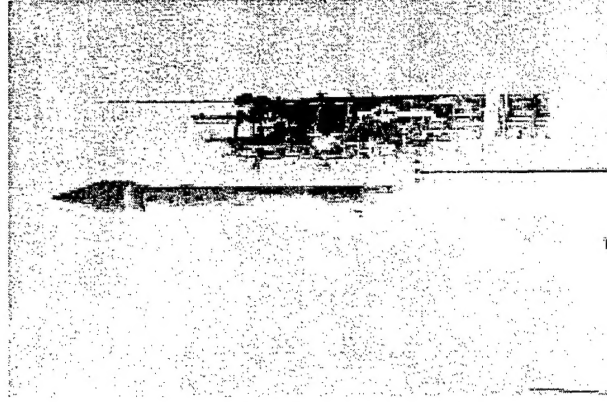
# HEDM Program Objective

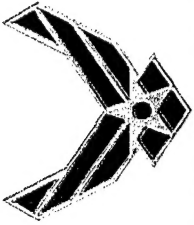


*Breaking the  
performance barrier*

Identify and develop advanced chemical propellants for rocket propulsion applications

- Hydrocarbons for liquid boosters
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for upper stages and satellites





# Current State of the Art



## Monopropellants

Hydrazine ( $N_2H_4$ )      Isp (sec)      Density ( $g/cm^3$ )      1.01

Hydrogen Peroxide ( $H_2O_2$ )      175      1.41

## Solids

Ammonium Perchlorate (AP)      260      1.69

~20%Al/~10% polymer binder

## Liquids

$N_2O_4$ /Hydrazine      280      1.45/1.01

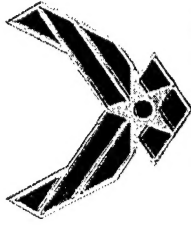
RP-1/Liquid Oxygen (LOX)      300      0.81/1.15

## Cryogenic

Liquid Hydrogen (LH2)/LOX      390      0.07/1.15

$I_{sp}$  at sea level 1000 psi chamber pressure

Isp = (pounds of thrust/pounds of propellant/second)



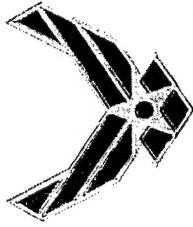
# HEDM Propellant Payoffs

***"The highest leverage technology area impacting launch vehicles is the development of high-energy-density materials for use as propellants."***

**-- New World Vistas Panel on Space Technology (1995)**

Vehicle Type	Baseline Vehicle	Propellant	Takeoff Mass (lb)	Payload Mass (lb)	Payload Mass (lb) With 10% Isp Increase
Two-stage ELV	Atlas II // Centaur D-1A	RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)	360,000	12,500	15,600 (+25%)
SSTO RLV	Lockheed SSTO	LH2/LOX (Isp = 455 s)	1,900,000	40,000	68,000 (+70%)
Missile Defense Interceptor	Boost-Phase Interceptor	HTPB/Al/HMX (Isp = 270 s)	1,847	74	110 (+49%)

***Our research is aimed at increasing propellant Isp by 5 to 50%***

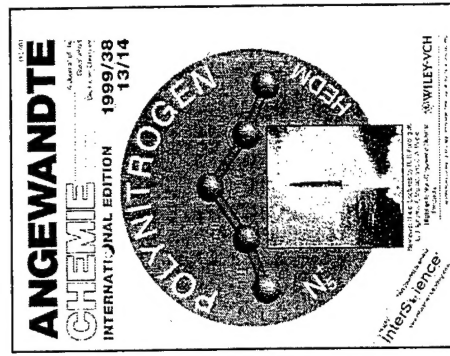
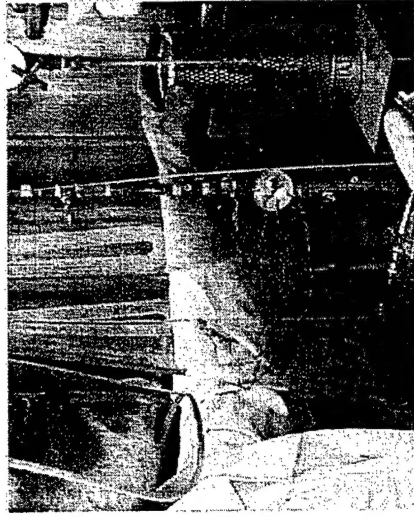
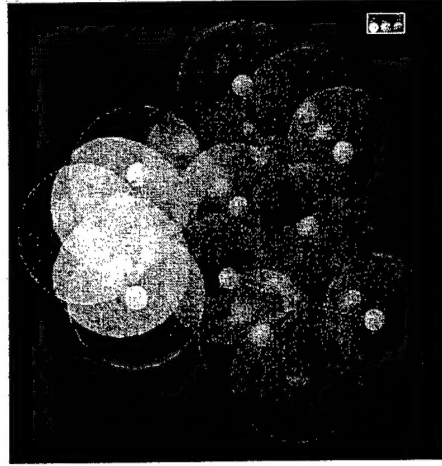


# Polynitrogen Project

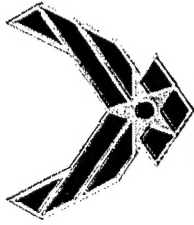
**Discover, synthesize, characterize, and scale-up novel, highly energetic polynitrogen allotropes**

*Modeling and simulation guides the experimental program:*

- ◆ Determines which molecules should exist and how energetic they are
- ◆ Gives information on how to synthesize promising molecules
- ◆ Provides critical data for identification and characterization of new molecules



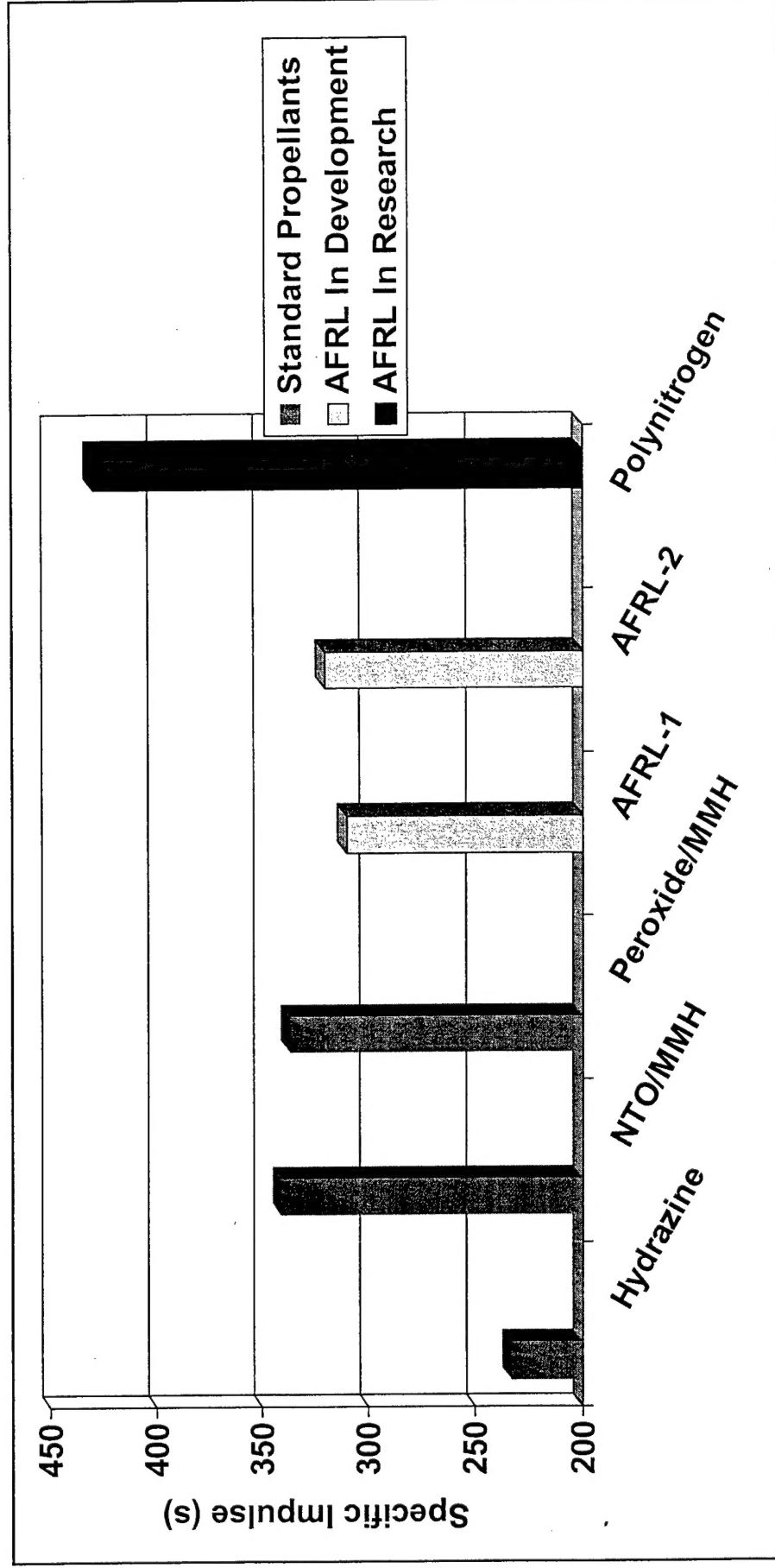




# Performance of Polynitrogen Monopropellants



*The performance of polynitrogens as monopropellants would dwarf that of hydrazine, and would greatly exceed even bipropellants*



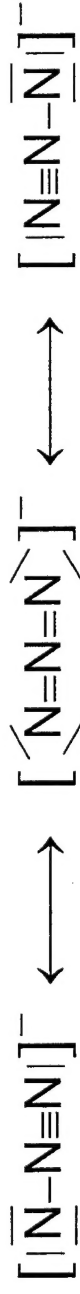




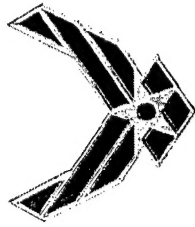
# The Search for New Polynitrogens

- All polynitrogens are unstable with respect to  $N_2$  molecules
- Their activation energy for  $N_2$  elimination is largely determined by the weakest bond in the compound

- Their metastability is enhanced if suitable resonance structures exist:

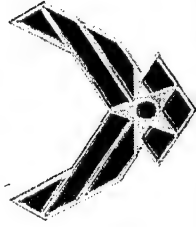


- The double-bond character of the  $\text{N}=\text{N}$  bonds in the azide anion explains its exceptional stability
- How can this stabilization effect be used to our advantage in preparing new compounds?

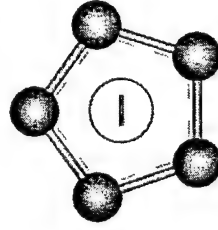


# Pentazolate ( $N_5^-$ )?

- Substituted pentazoles  $R-N_5$  have been known for decades ( $R=\text{aryl}$ )
- Cyclic  $N_5^-$  is aromatic
- Conversion of the diazonium salt,  $RN_2^+$ , to the substituted pentazole ring  $R-N_5$  by the reaction with azide ion,  $N_3^-$ , has been demonstrated many years ago by Ugi and Huisgen.
- $N_5^-$  has been recently detected in the gas phase for the first time, using collisional fragmentation (electrospray ion mass spectroscopy).
- Can a chemical route to  $N_5^-$  be found? (e.g., can a suitable R group be found for the reaction  $R-N_2^+ + N_3^- \rightarrow R-N_5 \rightarrow R^+ + N_5^-$ ?)

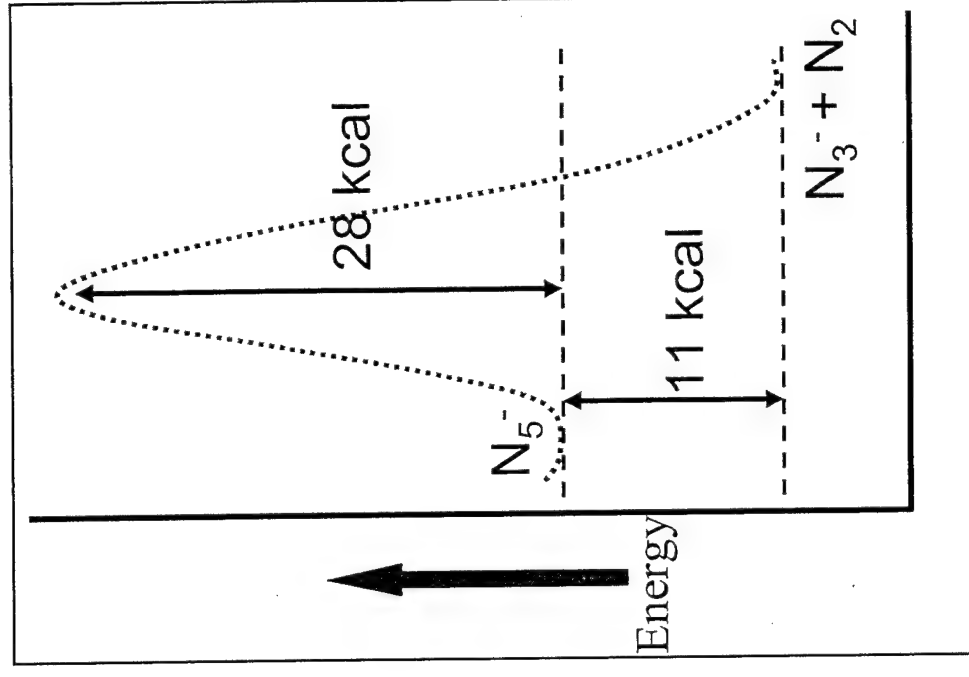


# New Polynitrogen Anions



## Pentazole anion ( $N_5^-$ )

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to  $N_3^-$  and  $N_2$  is only 11 kcal/mol exothermic
- Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and  $N_2$  gas

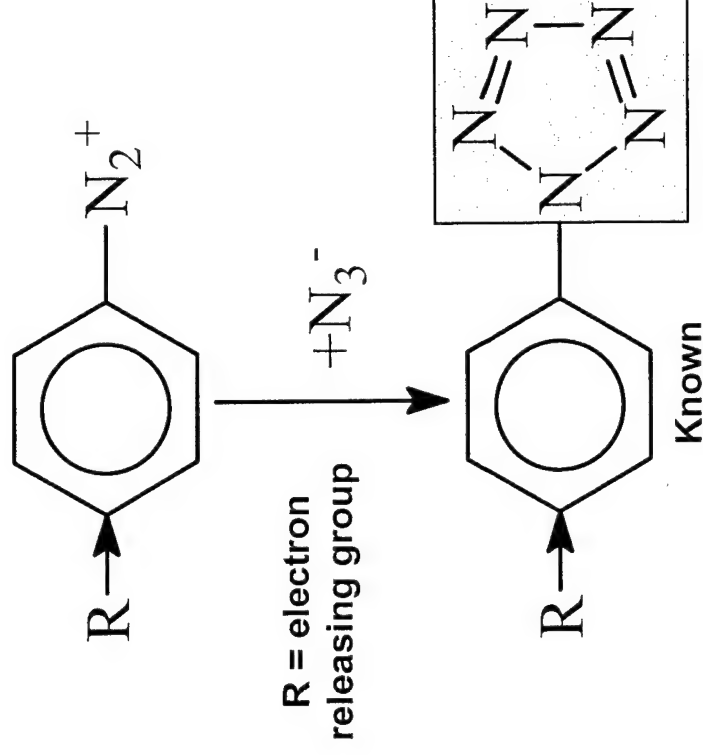
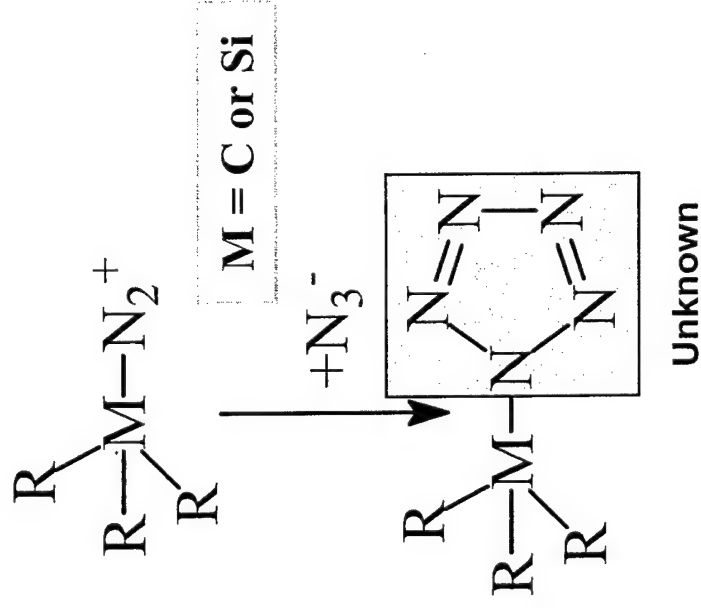
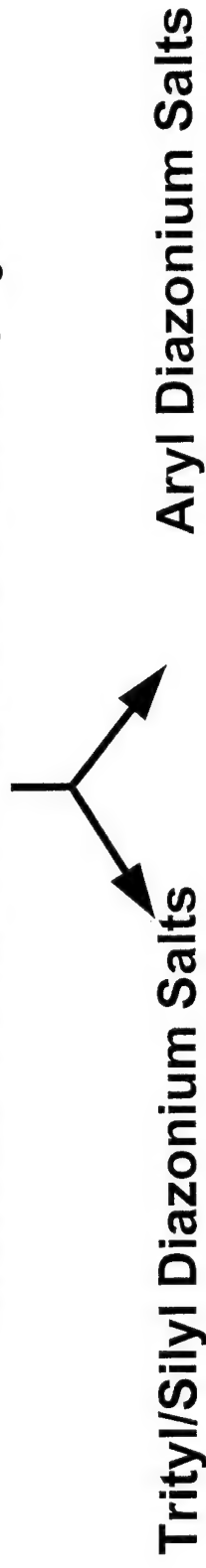




# Synthetic Challenge – How do we make These New Anions??

## Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion ( $N_5^-$ )





# Theoretical Challenge - Can we design and predict viable precursors to $N_5^-$ ?

Find a substituent R so that

1.  $R-N_2^+$  is stable wrt  $R^+ + N_2$ .
2. The R-N bond in  $R-N_5$  is weak, thereby suitable for the reaction  $R-N_5 + M^+X^- \rightarrow M^+N_5^- + R-X$

## Approach

Use quantum chemical calculations to predict the stability of  $R-N_2^+$  diazonium salts and the length/strength of the  $R-N_5$  bond.

MBPT(2)/6-31G(d) level of theory

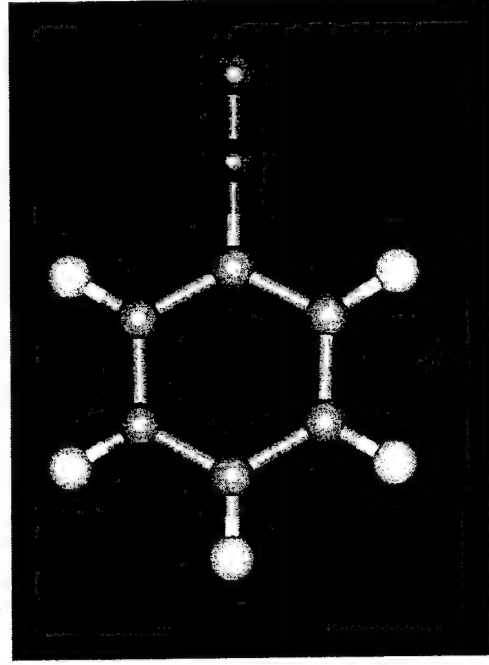


$M = C, Si$

$L = F, Cl, CH_3, CF_3, NO_2, phenyl, etc.$

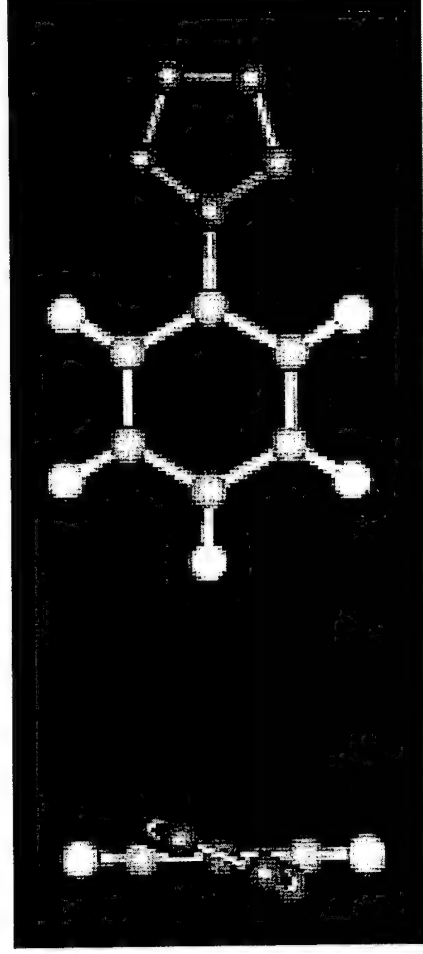


# Phenyldiazonium -- too stable!



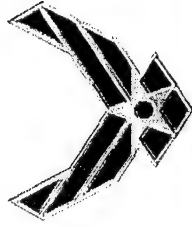
$$R(\text{C-N}_2^+) = 1.39 \text{ \AA}$$

$$D_e = 37.9 \text{ kcal/mol}$$

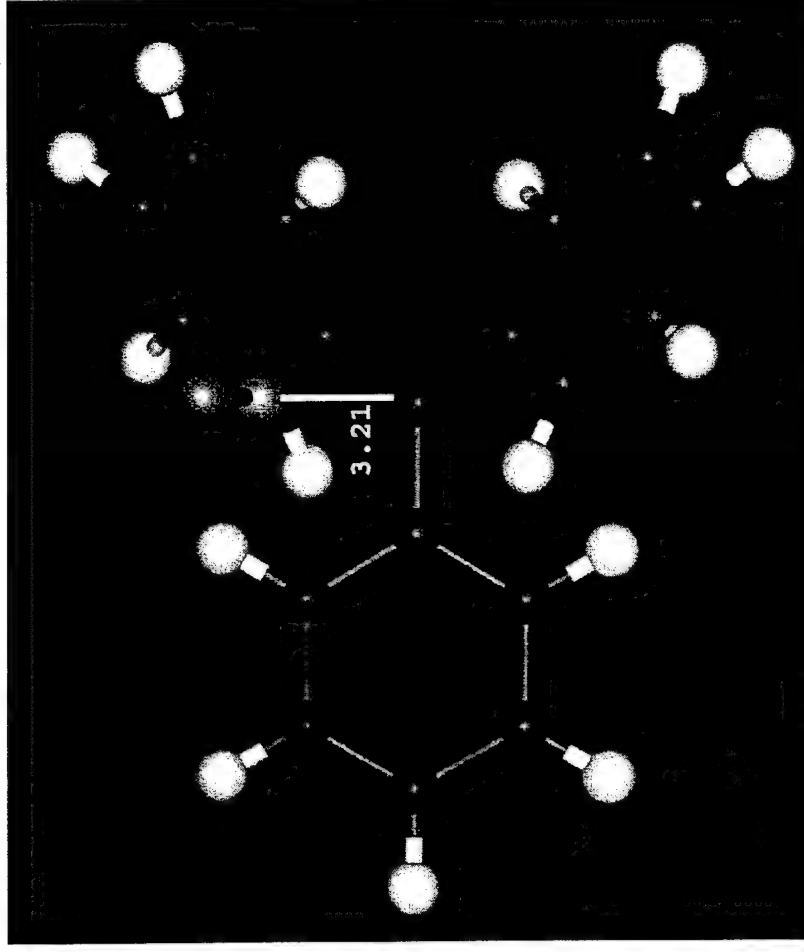
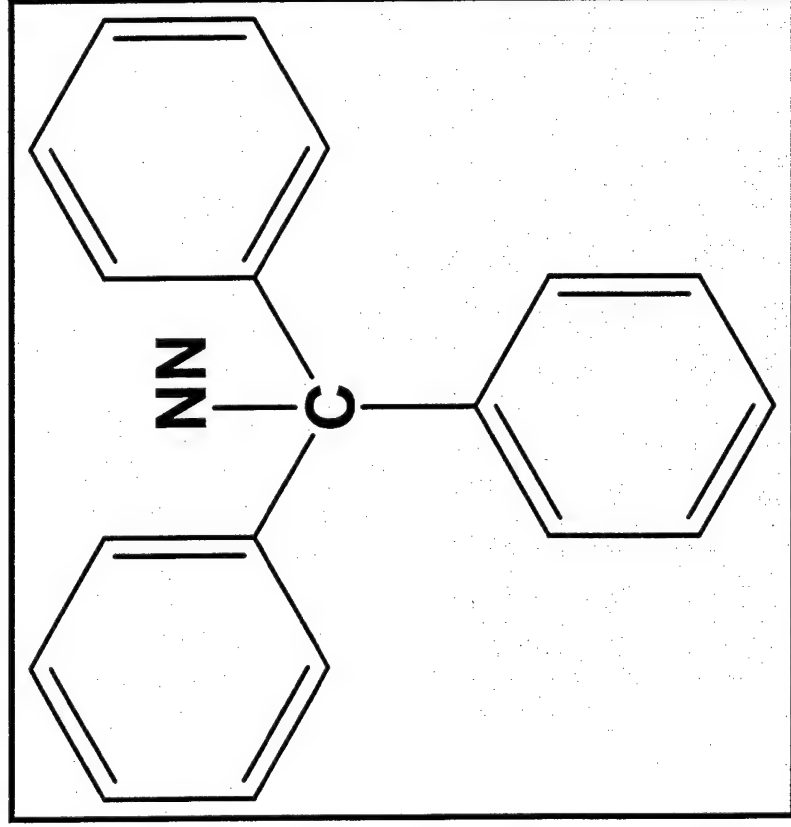


$$R(\text{C-N}_5) = 1.43 \text{ \AA}$$

Try replacing  $\text{Ph}^+$  with a more stable cation ( $\text{Ph}_3\text{C}^+$ )...

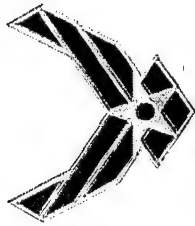


# ***Trityldiazonium -- unstable!***

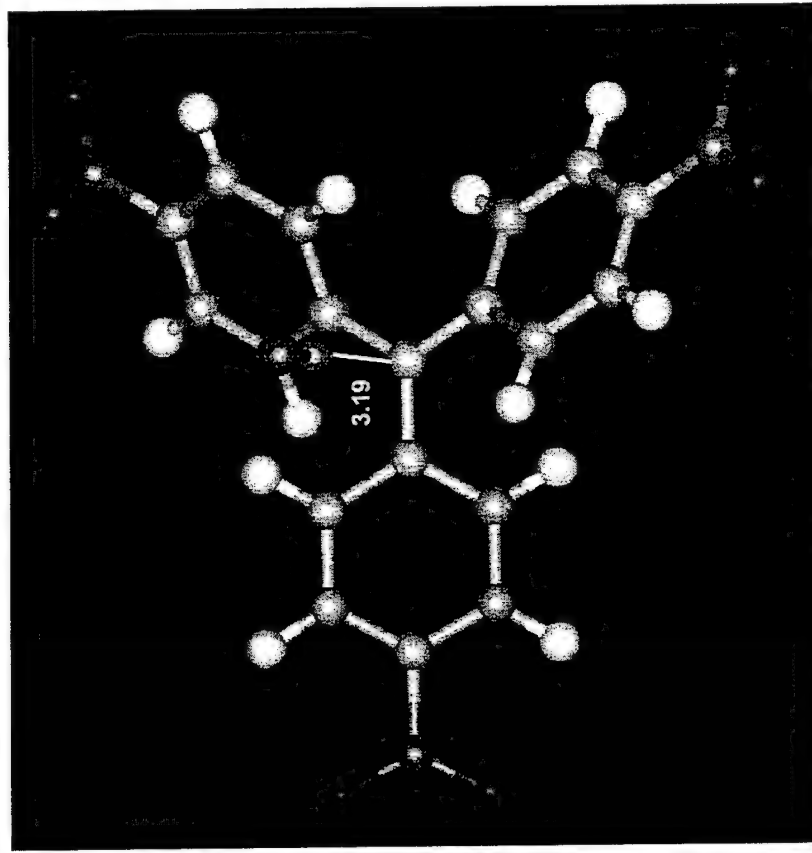


Trityl cation  $\text{Ph}_3\text{C}^+$  is too stable -- can it be destabilized by placing e-withdrawing groups on the phenyl rings (e.g.  $\text{NO}_2$ )?





# *tris(para-nitrophenyl) methylidiazoniumium*

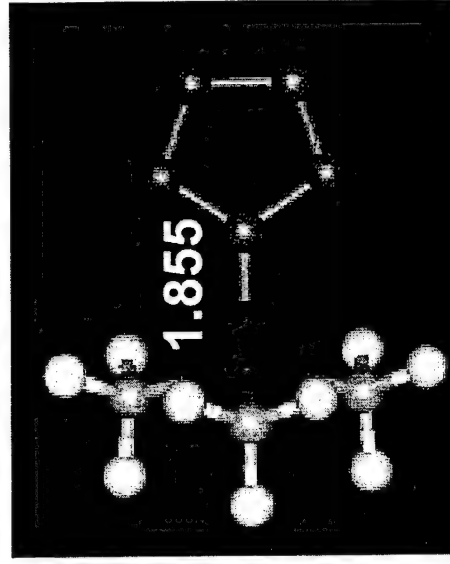
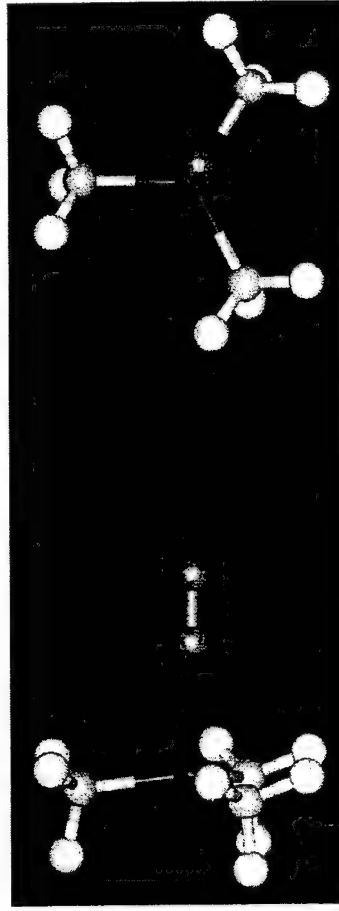
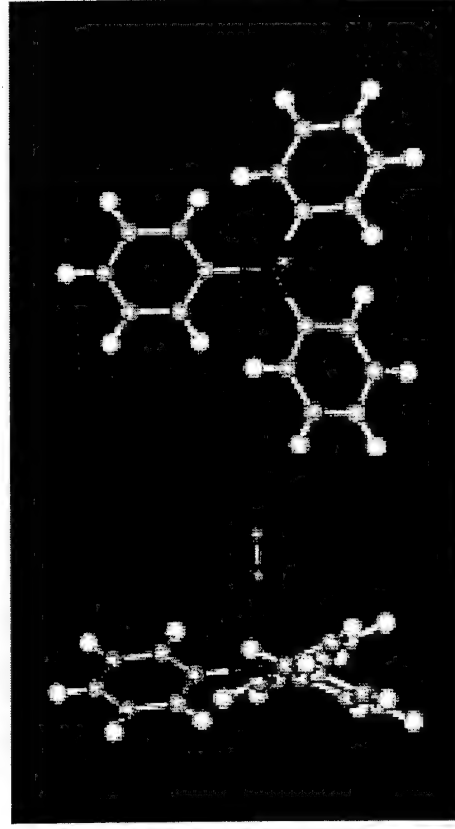


$R_3$	$R_3C-N_2^+$ distance(Å)	$D_e(C-N_2^+)$ (kcal/mol)
3Ph	> 3.0	-3.0
3(pNO <sub>2</sub> -Ph)	> 3.0	-3.4



# What about some silicon analogues?

$R_3$	$R_3Si-N_2^+$ distance(Å)	$D_e(Si-N_2^+)$ (kcal/mol)
3Ph	> 2.5	-6.0
3Me	2.151	-13.8

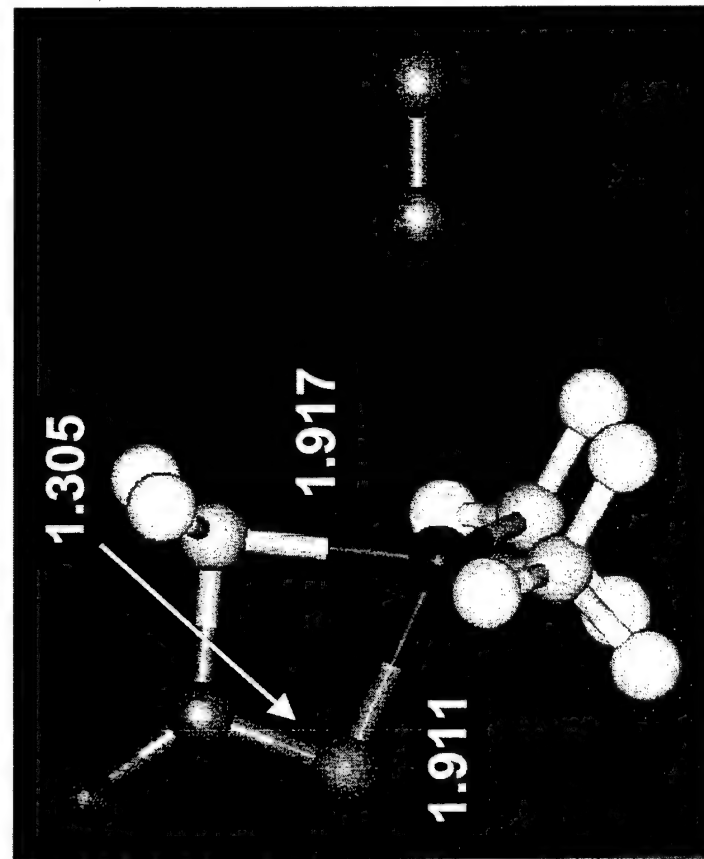
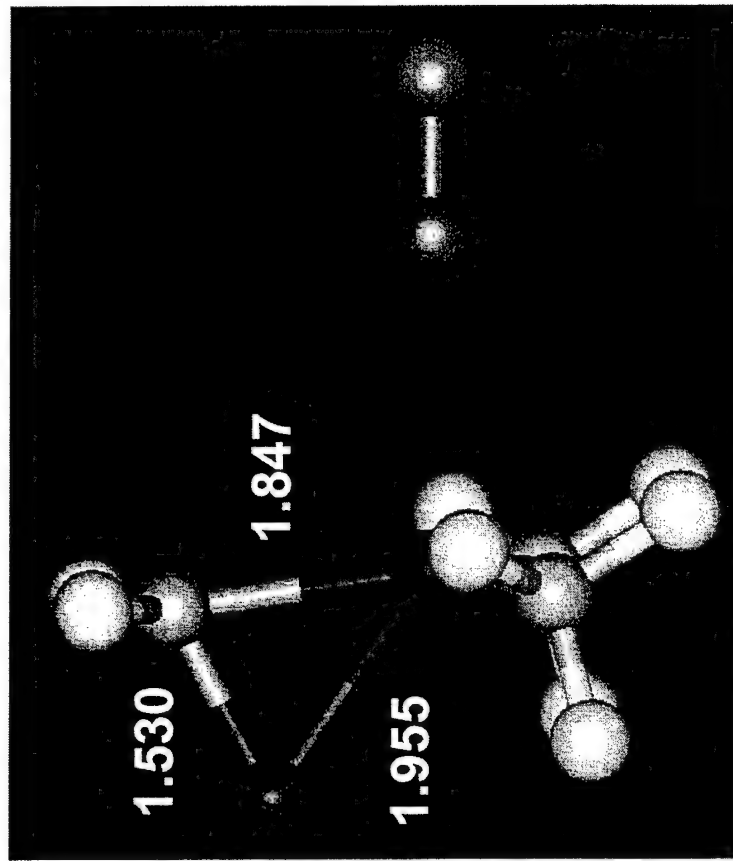


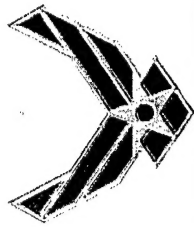
Trimethylsilyl cation looks promising --  
can it be “fine-tuned” to give a slightly  
more stable Si-N bond?



# Derivatives of trimethylsilyldiazonium

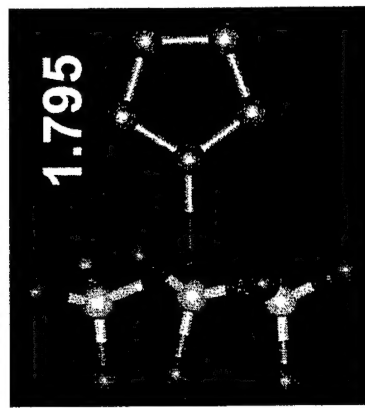
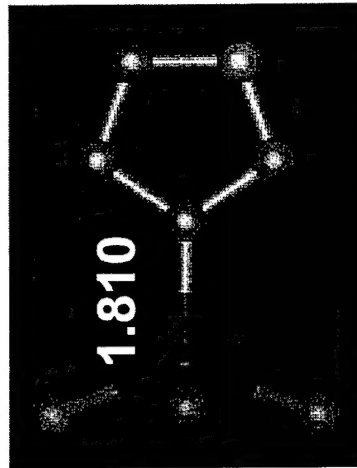
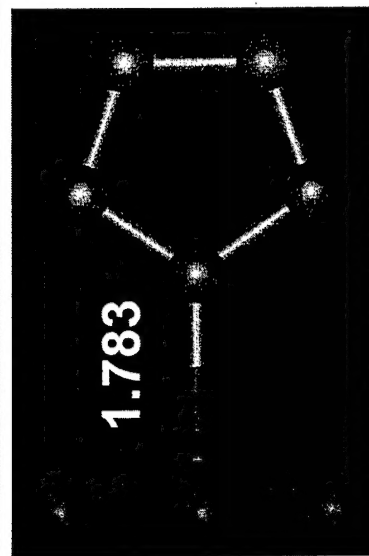
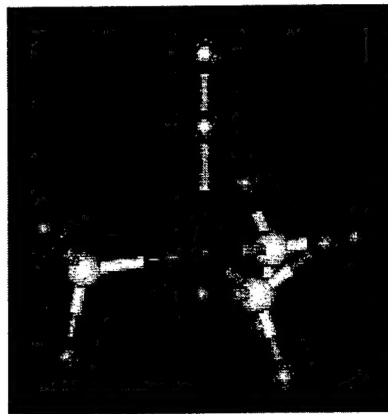
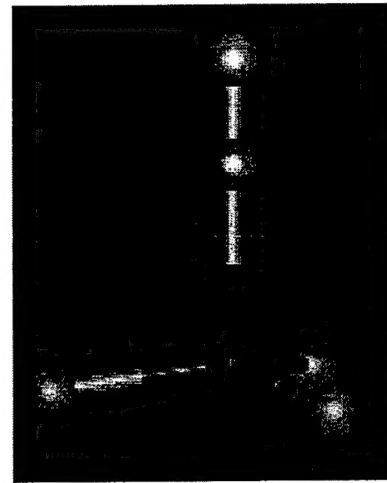
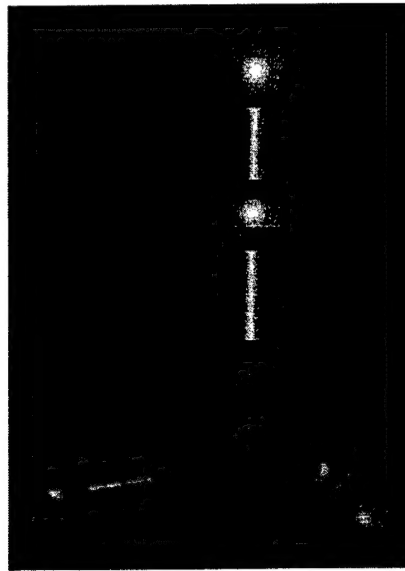
$R_3$	$R_3Si-N_2^+$ distance(Å)	$D_e(Si-N_2^+)$ (kcal/mol)
2Me,FCH <sub>2</sub>	2.410	-7.4
2Me,NO <sub>2</sub> CH <sub>2</sub>	> 2.5	-5.2





## Silicon analogues, continued

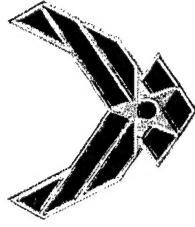
$R_3$	$R_3Si-N_2^+$ distance(Å)	$D_e(Si-N_2^+)$ (kcal/mol)
3F	1.973	-33.4
3Cl	2.125	-14.5
$3CF_3$	1.994	n/a





## Conclusions

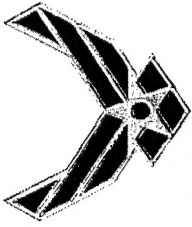
- Trityldiazonium ( $\text{Ph}_3\text{C-N}_2^+$ ) and its tris(para- $\text{NO}_2$ ) analogue are predicted to be unstable wrt dissociation of  $\text{N}_2$
- $\text{Ph}_3\text{Si-N}_2^+$  is also predicted to be unstable wrt dissociation of  $\text{N}_2$
- $\text{Me}_3\text{Si-N}_2^+$  and  $\text{Cl}_3\text{Si-N}_2^+$  are marginally stable ( $D_e \sim 14$  kcal/mol;  $R(\text{Si-N}) \sim 2.1$  Å)
- Of the silyl derivatives considered,  $\text{F}_3\text{Si-N}_2^+$  is the most stable ( $D_e = 33.4$  kcal/mol;  $R(\text{Si-N}_2^+) = 1.97$  Å)
- Secondary (i.e., not directly bonded to Si) electronegative groups such as F and  $\text{NO}_2$  interact strongly with Si in silyldiazonium cations, leading to displacement of  $\text{N}_2$



## ***Future/ongoing work***



- Calculation of the structures and stabilities of  $\text{Me}_x\text{F}_y\text{Cl}_z\text{Si-N}_2^+$  and  $\text{Me}_x\text{F}_y\text{Cl}_z\text{Si-N}_5$
- Calculation of the reaction enthalpies  $\text{R-N}_5 + \text{M}^+\text{X}^- \rightarrow \text{M}^+\text{N}_5^- + \text{R-X}$
- Other high-nitrogen/polynitrogen species (e.g.  $\text{Fe}(\text{N}_5)_2$ )



## *Acknowledgements*

---

**DARPA, AFOSR, AFRL**

**DoD HPC Modernization Program**

**New Materials Design Challenge Project**

**Aeronautical System Center**

**AFFTC Distributed Center**

**Army HPC Research Center**

**Common HPC Software Support Initiative**

**Dr. Robert Corley (AFRL)**